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- (71) Applicant: CANON KABUSHIKI KAISHA Ohta-ku, Tokyo (JP)
- (72) Inventor: Maehara, Hiroshi Ohta-ku, Tokyo (JP)
- (74) Representative: Weser, Wolfgang, Dr. Dipl.-Phys. Weser & Kollegen, Patentanwälte, Radeckestrasse 43 81245 München (DE)
- (54) Resin composition, method of molding the same, and method of recycling resin composition
- (57) A resin composition which comprises a biodegradable polymer and a biodegradable liquid crystalline polymer. The resin composition is useful for producing molded resin articles having good recyclability.

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Description

BACKGROUND OF THE INVENTION

5 Field of the Invention

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[0001] The present invention relates to a resin material of low environmental loading in consideration of global environment. The present invention also relates to a method of recycling the resin composition for material circulation to build a recycling society.

Related Background Art

[0002] Mankind has successively created various materials useful for daily lives and industries through the coal chemistry age and the petroleum chemistry age. In particular, the symbolic example is synthetic polymer resins including plastic materials such as polyethylene, polypropylene, and polyvinyl chloride; and rubbers such as polyisoprene, and polybutadiene. Recently, novel resin materials having excellent properties have been developed, including polyimide resins and all-aromatic liquid crystalline polymers having high heat resistance and high impact strength.

[0003] In recent years, however, in the industrial structure based on the mass production, mass consumption, and mass waste, discarded polymers cause problems. Specifically, the discarded materially stable polymer materials remain undecomposed in the soil for a long term, gradually releasing endocrine disrupters and other harmful substances to result in serious adverse effects on living things occasionally. When the polymer materials are incinerated, toxic materials such as dioxin can be generated depending on the incineration conditions to cause extreme danger. Another waste material is a large amount of waste paper discharged from offices, which also causes environmental problems. [0004] Under such circumstances, materials and products which do not destruct the environment are wanted. Further, technical development is required which enables conservation of the environment by minimizing the consumption of global resources and recycling the materials.

[0005] On the other hand, one of the general methods for improving the properties of the polymer is introduction of a fiber structure into a polymer by blending a foreign material. Generally this method includes blending of an inorganic material such as glass fiber, and carbon fiber; blending of an organic polymer fiber such as nylon fiber, and polyester fiber; and blending of a liquid crystalline polymer having high orientability. For example, U.S. Patent 6,248,267 discloses a natural-fiber-containing nonwoven fabric. Lately the amounts of industrial waste materials and household waste materials are increasing, and the disposed materials are causing a social problem. Generally, organic polymer materials such as polyethylene and polypropylene are stable, and once discarded, they will persist in the soil for a long term. To avoid such a problem, the use of a biodegradable polymer materials is considered. However, biodegradable polymers do not have satisfactory properties in the broad range of application fields in comparison with the versatile polymer materials. The properties of a biodegradable polymer can be improved by blending of the aforementioned fiber material. However the blended filler, which is not biodegradable, renders the recycling difficult, resulting in increase of environmental loading by the persistence in the environment for a long term after the disposal.

40 SUMMARY OF THE INVENTION

[0006] The present invention intends to provide a resin composition useful for production of molded resin articles which can be readily recycled without remaining after disposal.

[0007] The resin composition of the present invention comprises a biodegradable polymer and a biodegradable liquid crystalline polymer.

[0008] The process of producing a molded resin article of the present invention comprises molding the above resin composition at a molding temperature not higher than the liquid crystal transition temperature of the liquid crystalline polymer contained in the resin composition.

[0009] The molded resin article of the present invention is obtained by molding the above resin composition.

[0010] The method of reusing waste paper of the present invention comprises the steps of producing at least one of a biodegradable polymer and a liquid crystalline polymer from the waste paper, and producing a resin composition of the above composition by use of the at least one polymer.

[0011] The method of recycling the resin composition having the above composition comprises decomposing the molded resin article composed of the resin composition to obtain a decomposition product, recovering at least one of the aforementioned biodegradable polymer and the aforementioned liquid crystalline polymer from the decomposition product, and reusing the above obtained at least one polymer for production of the resin composition.

[0012] The present invention provides a resin composition useful for producing a molded resin article which does not persist after disposal and is readily recyclable. In particular, the resin composition of the present invention can be

produced by use of a component derived from waste paper. When the molded article of this resin composition is discarded after use, the polymer component can be recycled by recovering the polymer component from the discarded molded resin article.

5 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

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[0013] The resin composition of the present invention contains at least a biodegradable polymer and a biodegradable liquid crystalline polymer. The resin composition of the present invention can be composed of only biodegradable components. Such a polymer does not cause the persistency problem after disposal, and can be recycled readily. The liquid crystalline polymer can give an oriented polymer molecule structure to the molded article to improve the mechanical strength of the molded article.

[0014] The biodegradable polymer employed is selected from those which are biodegradable and not liquid-crystal-line, and preferably contains a sugar structure. The polymer having a sugar structure includes polymers having a sugar structure such as starch cellulose, chitin, chitosan, pullulan, and curdian; copolymers of D-glucose with an aliphatic dicarboxylic acid such as malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and sebacic acid; copolymers of D-glucose with an aromatic dicarboxylic acid such as terephthalic acid, isophthalic acid, naphthalene dicarboxylic acid, and naphthalic acid; and copolymers with another compound such as polyether, polyvinyl alcohol, polymalic acid, polyhydroxyalkanoate, and polylactic acid. The biodegradable polymer selected from the above-mentioned polymers may be used singly or in combination of two or more thereof, as necessary. Of these, preferred are those containing glucose as the sugar component.

[0015] The biodegradable polymer preferably has a molecular weight (weight average) ranging from 100,000 to 5,000,000.

[0016] On the other hand, the biodegradable liquid crystalline polymer preferably has biodegradability, and has characteristics of a liquid crystal in a solution or in a molten state, and has an orientational structure.

[0017] Such a liquid crystalline polymer includes cellulose and polymers having an alkyl group on the side chain of a cellulose derivative. Examples thereof are described, for instance, in "Miyamoto, Yamagishi: Kobunshi Kako, 38, 12, (1989)", and "S.Tseng et al.: Macromolecules, 15, 1262 (1982)". Formulas (1) to (3) shows typical examples the polymer:

wherein R1, R2, and R3 independently denote hydrogen, or an aliphatic ester of 1 to 10 carbon atoms;

wherein R4. R5, and R6 independently denote hydrogen or an alkyl group of 1 to 10 carbon atoms; and

wherein R7, R8, and R9 independently denote hydrogen or a hydroxyalkyl group of 1 to 10 carbon atoms.

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[0018] The cellulose derivative includes methylcellulose, ethylcellulose, carboxymethylcellulose, hydroxyethylcellulose, and hydroxypropylcellulose. The alkyl group is introduced by directly bonding an alkyl group by utilizing the three hydroxyl groups of D-glucose, a repeating unit of the cellulose molecule; by bonding an alkyl group by utilizing the hydroxyl group of hydroxyethylcellulose or hydroxypropylcellulose, by utilizing the lower alkyl groups of a cellulose derivatives such as methylcellulose, ethylcellulose, and carboxymethylcellulose, or utilizing the remaining hydroxyl groups of these compounds. The alkyl group can be bonded to the cellulose or the cellulose derivative through ester bonding, ether bonding, amide bonding, or the like. Specific examples include hydroxyalkylcellulose such as hydroxyethylcellulose and hydroxypropylcellulose, and reaction products of hydroxyalkylcellulose with an aliphatic carboxylic acid such as acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, enanthic acid, caprylic acid, pelargonic acid, capric acid, undecylic acid, lauric acid, and tridecanedioic acid. Hydroxypropylcellulose is particularly preferred as the cellulose derivative for the alkyl group introduction. The liquid crystalline polymer may be employed singly or in combination of two or more thereof.

[0019] In the above Chemical Formulas (1) to (3), the degree of substitution by a substituent other than hydrogen is not lower than 20% in a molecule to develop the liquid crystal properties.

[0020] The molecular weight (weight average) of the liquid crystalline polymer ranges, for example, from about 100,000 to about 5,000,000, but is not limited thereto.

[0021] The liquid crystal transition temperature of the liquid crystalline polymer can be varied depending on the type of the alkyl group or the reaction degree in the alkyl group introduction. This temperature characteristics can be selected in consideration of the molding temperature of the blending polymer. For example, in the case where a copolymer of D-glucose and sebacic acid having a molding temperature of about 110°C is used as the biodegradable polymer, a reaction product of hydroxyethylcellulose and butyric acid is preferably used as the liquid crystalline polymer. At a degree of the substitution of 70% of hydroxyethylcellulose with butyric acid, the liquid crystal transition temperature of the reaction product is 135°C. This temperature is nearly equal to the molding temperature of the above polymer.

[0022] In blending the biodegradable polymer and the liquid crystalline polymer, the blending ratio (A)/((A)+(B)), where (A) represents the mass of the biodegradable polymer and (B) represents the mass of the liquid crystalline polymer, ranges preferably from 0.05 to 0.95.

[0023] The resin composition of the present invention is obtained by filling or blending of the liquid crystal polymer into the biodegradable polymer. The mixing of these components can be conducted by any known method.

[0024] Incidentally, use of cellulose or the like recovered from paper, especially waste paper, as the source material for the biodegradable polymer or liquid crystalline polymer can increase the recyclability of waste paper. Any known process can be employed for producing the polymer component for the resin composition from waste paper.

[0025] The simple mixture of the biodegradable polymer and the liquid crystalline polymer can be used as the resin composition. If necessary, an additive may be incorporated thereto provided that the object of the present invention is achievable. The additive includes plasticizers, pro-oxidant, age resistor, crosslinking agents, surfactants, and compatibilizing agents. The additive should be selected which causes minimum environmental loading. In use of the material in a closed system where the material is completely recycled, a usual additive may be used.

[0026] The application field of the resin composition is not limited specially. The resin composition is useful, for example, as constituent materials for ink tanks of ink-jet printers, toner containers of electrophotography apparatuses, packing materials, casings of printers and cameras, transparency sheets, and so forth.

[0027] The processing and molding conditions of the resin composition of the present invention are selected depending on the properties of the biodegradable polymer and the liquid crystalline polymer to be combined. In the case

where the biodegradable polymer is thermoplastic or thermally fusible, the molding conditions and press conditions are selected depending on the softening point, glass transition temperature, melting point, and the like thereof. The molding temperature is preferably set at a temperature not higher than the liquid crystal transition temperature of the liquid crystalline polymer, as described above. The resin composition can be molded by various molding processes including injection molding, and extrusion molding.

[0028] The molded article obtained from the resin composition of the present invention can be recycled effectively after it is discarded. For example, the molded article is decomposed by acid treatment, or high-temperature and high-pressure water treatment; the polymer components are recovered from the resulting decomposition product; and the polymer component is used as at least one source material of the resin composition of the present invention.

<Examples>

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[0029] The present invention is described below in more detail by reference to examples. The unit "percent (%)" is based on mass.

(Example 1)

(Reaction of Hydorxyethylcellulose and butyric acid)

20 [0030] In a four-neck separable flask equipped with a refluxing device and a stirrer, was placed 39.3 g of butyric acid. Nitrogen gas was bubbled therein for one hour to replace the dissolved oxygen. Thereto 50 mL of trifluoroacetic anhydride was added gradually under a nitrogen gas flow. The temperature was elevated gradually up to 50°C by a water bath, and the activation was conducted for 30 minute. Therein 4.6 g of dried solid hydroxyethylcellulose was added gradually through an inlet: the polymer was dissolved quickly. Under this state, the reaction was continued further for 5 hours. After the reaction, the reaction mixture was poured into a large amount of water to precipitate a butyric acid ester of hydroxyethylcellulose. The obtained polymer was dried, and purified by repetition of re-dissolution in acetone and reprecipitation in water. The yield of the polymer was 6.1 g.

[0031] The obtained polymer (weight-average molecular weight: 350,845) was confirmed to be the intended substance by IR absorption spectroscopy and NMR, and found to have a liquid crystal transition temperature of 135°C by thermal analysis.

(Example 2)

(Reaction of Hydroxypropylcellulose and lodobutane)

[0032] In a sufficiently dried four-neck separable flask equipped with a refluxing device and a stirrer, hydroxypropyl-cellulose (hereinafter, HPC) was dissolved in THF, and thereto a solution of n-butyllithium in hexane was added. After stirring for 30 minutes, the mixture was heated to 66°C, and thereto iodobutane was added dropwise while refluxing the THF. The mixture was allowed to react for 10 hours.

[0033] After the reaction, the reaction product was precipitated in deionized water to obtain a butyl ether compound of HPC. The obtained polymer was purified by repetition of dissolution in acetone and precipitation in deionized water. [0034] The obtained polymer (weight-average molecular weight: 475,000) was confirmed to be the intended substance by IR absorption spectroscopy and NMR, and found to have a liquid crystal transition temperature of 125°C by thermal analysis.

(Example 3)

[0035] In a sufficiently dried four-neck separable flask equipped with a refluxing device and a stirrer, industrial alkalicellulose was caused to react with butyl iodide in DMSO solution to produce cellulose butyl ether. After the reaction, the reaction product was precipitated in deionized water to obtain a cellulose butyl ether compound. The obtained polymer was purified by repetition of dissolution in acetone and precipitation in deionized water.

[0036] The obtained polymer (weight-average molecular weight: 255,000) was confirmed to be the intended substance by IR absorption spectroscopy and NMR, and found to have a liquid crystal transition temperature of 160°C by thermal analysis.

(Example 4)

[0037] The polymer obtained in Example 1 was dissolved in cyclohexanone with a concentration of 5%. The solution

was spin-coated on a glass substrate at a rotation speed of 3000 rpm. This substrate was observed by polarizing microscopy to confirm the molecular orientation state.

(Example 5)

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[0038] An acetone solution of the polymer obtained in Example 2 was dropped onto a glass substrate and was dried. This substrate was placed on a hot plate kept at 130°C. With another glass substrate, the polymer was pressed while applying a shear stress. Then the substrate was transferred onto a cooled metal plate to cool the polymer. After cooling, the polymer was observed by polarizing microscopy to confirm molecular orientation in the direction of the force application.

(Example 6)

[0039] A DMSO solution of the polymer obtained in Example 3 was dropped onto a glass substrate and was dried. This glass substrate was placed on a hot plate kept at 170°C. With another glass substrate, the polymer was pressed while applying a shear stress. Then the substrate was transferred onto a cooled metal plate to cool the polymer. After cooling, the polymer was observed by polarizing microscopy to confirm molecular orientation in the direction of the force application.

20 (Example 7)

[0040] The polymer obtained in Example 1 was blended in a blending ratio of 20% with a glucose-sebacic acid copolymer which is a biodegradable resin and has a weight-average molecular weight of 50,000 to prepare a resin composition. This resin composition was molded by an injection molding machine at 140°C. The molded sample had a tensile strength improved by a factor of 1.5 in comparison with the glucose-sebacic acid copolymer before blending. The orientation of the resin was confirmed by observation of the broken-out section with electron microscopy.

(Example 8)

- 30 [0041] The polymer obtained in Example 1 was blended with a blending ratio of 25% with polylacetic acid which is a biodegradable resin and has a weight-average molecular weight of 150,000 to prepare a resin composition. This resin composition was molded by an injection molding machine at 140°C. The molded sample had a tensile strength improved by a factor of 2 in comparison with the polylacetic acid before blending.
- 35 (Example 9)

[0042] A polymer was synthesized in the same manner as in Example 3 except that a cellulose material separated from waste paper was used in place of the industrial cellulose as the source material. The obtained polymer was similar to the polymer obtained in Example 3 in appearance and properties.

(Example 10)

[0043] A transparency sheet was prepared by blending the butyl ester of hydroxyethylcellulose (HEC) obtained in Example 1 with polylactic acid, and press-molding the resulting blend. This sheet has excellent transparency because of no light absorption in the visible light region. This sheet was compatible with ink and had excellent printability since this sheet is based on cellulose source material. Furthermore, owing to a single layer structure of the sheet formed from the resin composition of the present invention, this sheet did not cause curling or other deformation which may be caused in multilayered sheets due to difference in thermal expansion coefficients at temperature rise.

50 (Example 11)

[0044] The transparency sheet molded in Example 10 was shredded into chips by a shredder. The sheet chips were decomposed by action of fuming hydrochloric acid (at a temperature of 25°C), or high-temperature and high-pressure water (at a pressure of 35 MPa and a temperature of 400°C). The glucose chemically separated from the decomposition product was used as a source material for synthesis of glucose-sebacic acid copolymer.

(Example 12)

[0045] The transparent sheet molded in Example 10 was melted and pressed again to mold a transparency sheet. This sheet was found to be usable as a transparency sheet without causing problem in light transmissivity and other properties.

(Example 13)

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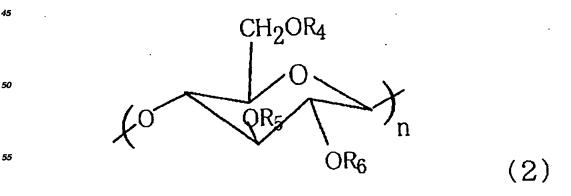
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[0046] The transparency sheet molded in Example 10 was melted, and pelletized, and was molded by an injection machine into a casing of an ink-jet printer. The casing was formed without problem in molding.

Claims

- 15 1. A resin composition, comprising a biodegradable polymer and a biodegradable liquid crystalline polymer.
 - 2. The resin composition according to claim 1, wherein the biodegradable polymer comprises a sugar structure.
 - 3. The resin composition according to claim 2, wherein the sugar structure contains glucose.
 - 4. The resin composition according to claim 3, wherein the structure containing glucose is a structure in which the glucose and a dicarboxylic acid are bonded.
 - The resin composition according to claim 1, wherein the liquid crystalline polymer has a structure represented by Formula (1):

- 40 wherein R1, R2, and R3 independently denote hydrogen, or an aliphatic ester of 1 to 10 carbon atoms.
 - 6. The resin composition according to claim 1, wherein the liquid crystalline polymer has a structure represented by Formula (2):



wherein R4, R5, and R6 independently denote hydrogen or an alkyl group of 1 to 10 carbon atoms.

The resin composition according to claim 1, wherein the liquid crystalline polymer has a structure represented by Formula (3):

20 wherein R7, R8, and R9 independently denote hydrogen or a hydroxyalkyl group of 1 to 10 carbon atoms.

- 8. The resin composition according to claim 7, wherein the liquid crystalline polymer is hydroxypropylcellulose.
- 9. The resin composition according to claim 1, wherein a blending ratio of (A)/((A)+(B)) ranges from 0.05 to 0.95, where (A) represents the mass of the biodegradable polymer and (B) represents the mass of the liquid crystalline polymer.
- 10. The resin composition according to claim 1, wherein the liquid crystalline polymer has an orientation structure.
- 30 11. The resin composition according to claim 1, wherein at least one of the biodegradable polymer and the liquid crystalline polymer is derived from waste paper.
 - 12. A process for producing a molded resin article, comprising the steps of:
 - preparing a resin composition containing a biodegradable polymer and a biodegradable liquid crystalline polymer, and
 - molding the resin composition at a temperature not higher than the liquid crystal transition temperature of the liquid crystalline polymer.
- 40 13. A molded resin article, formed by molding a resin composition containing a biodegradable polymer and a biodegradable liquid crystalline polymer.
 - 14. A method of recycling waste paper, comprising the steps of:

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- producing at least one of a biodegradable polymer and a biodegradable liquid crystalline polymer, from waste paper, and
- producing a resin composition by using the at least one polymer produced.
- 15. A method for recycling a resin composition containing a biodegradable polymer and a biodegradable liquid crystalline polymer, comprising the steps of:
 - decomposing a molded article formed from the resin composition to obtain a decomposition product, recovering at least one of the biodegradable polymer and the biodegradable liquid crystalline polymer, and reusing the recovered at least one polymer for producing the resin composition.
- 16. The method according to claim 15, wherein the resin composition of the molded article is decomposed by treatment with an acid.

17.	The method according to claim 15, wherein the decomposition step of the molded article is carried out by a treatment with high-temperature and high-pressure water.
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Application Number EP 02 00 5976

Category	Citation of document with in of relevant pass	adication, where appropriate, ages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.CL7)	
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